

Determination of Rubber Hydrocarbon by a Gravimetric Rubber Bromide Method

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A direct method is given for determining rubber hydrocarbon in extracts from plant tissues, and in rubber crudes, latices, and liquors. The method is based upon the formation of an alcohol-insoluble rubber bromide whose composition varies slightly, depending on the source of the rubber. Gravimetric factors are established for converting weights of rubber bromide to weight of rubber, when the source is guayule, *Cryptostegia*, or *kok-saghyz*. Data are presented showing that reasonable variations in time and temperature of bromination and changes in concentration of rubber and brominating solution, within rather wide limits, do not appreciably alter the accuracy of the method.

DIRECT determination of rubber hydrocarbon in crude rubbers and in latices has been generally considered so inaccurate and unreliable that determination of rubber hydrocarbon by difference has been a common practice. The difference method usually suffices in the analysis of products derived from Hevea rubber, in which the nonrubber constituents have been well characterized or occur in low concentration. In the analysis of natural rubber products obtained from sources other than Hevea, such as guayule, *kok-saghyz*, and *Cryptostegia*, the situation is different. The chemical and physical properties of the nonrubber constituents of such products are largely unknown, and in many cases the nonrubber contaminants are present in excessive amounts, sometimes more than 50% of the total. Since the rubber hydrocarbon analysis usually affords the most reliable means for estimating the rubber content of plants and for following the concentration and purification of rubber by mechanical and chemical processes, it appeared desirable to devise or adapt a method which would permit direct determination of this constituent in the presence of relatively large amounts of natural and added contaminants.

Among the methods for determination of rubber in the literature, those which have received the largest amount of study are the gravimetric (1, 3, 5, 10, 12) and volumetric (7, 11, 13) methods based on the formation of the bromine derivative of rubber. Other methods are the empirical chromic acid oxidation (4), the direct alcohol precipitation (6), and the nitrosite procedures (9, 15). The gravimetric bromide method showed the greatest promise of adaptability to the determination of rubber hydrocarbon in a wide variety of rubber-containing products. Both the volumetric bromide method and the chromic acid oxidation method are subject to error when the rubber contains material other than rubber hydrocarbon, since any nonrubber compounds capable of reacting with bromine interfere in the volumetric bromide method and any constituents yielding volatile acids on digestion with chromic acid tend to give high results if the chromic acid oxidation method is employed. Estimation of rubber by direct weighing of the hydrocarbon precipitated with alcohol is not applicable to the determination of rubber in impure or dilute solutions. The nitrosite method was not investigated, since it has never met with favor because of the uncertain composition of the reaction products. The gravimetric bromide method was therefore selected for further investigation as a possible and practical means for the direct estimation of rubber hydrocarbon.

The bromine derivative of rubber or the so-called "tetrabromide" was first prepared by Gladstone and Hibbert (8), who isolated the compound by evaporating the solvent from a chloroform-rubber solution that had been treated with bromine. Weber (14) found that the compound could be more conveniently iso-

lated by precipitation with alcohol. Analysis of his preparation showed a composition in essential agreement with the formula $C_{10}H_{14}Br_4$. The methods devised for determination of rubber hydrocarbon based on the formation of the bromide vary in the choice of (a) rubber solvent (carbon tetrachloride, chloroform, or benzene), (b) brominating conditions such as time, temperature, and composition and concentration of the reagent, and (c) bromide precipitant (alcohol, acetone, or petroleum ether). In several of the methods the bromine in the isolated bromide precipitate is determined and the amount of rubber hydrocarbon calculated by using the ratio of 1 isoprene unit (C_5H_8) to 2 bromine.

Several early investigators recognized that this theoretical ratio was not obtained in practice, since formation of the bromide was generally accompanied by liberation of hydrogen bromide, indicating that substitution as well as addition of bromine took place. Hinrichsen and Kindscher (10) observed no liberation of hydrogen bromide if the bromination was carried out at 0° C., and proposed a method based on this finding. The volumetric bromide method of Lewis and McAdams (11) attempted to evaluate the amount of substitution by titration of the liberated hydrogen bromide and corrected the results accordingly. Bloomfield (2) has recently reported that when bromination of rubber is carried out at temperatures below 0° C. in a medium containing a trace of alcohol, substitution of bromine is minimized. A simple adaptation of the bromide method was made by Edison (5) and his associates for use in their survey of native American plants as potential sources of natural rubber. In this method, a benzene or carbon tetrachloride solution of rubber is brominated for one hour, the bromide is precipitated with alcohol, washed, dried, and weighed, and the rubber hydrocarbon content is calculated by multiplying the weight of recovered bromide by an empirical factor, 0.285, instead of the theoretical factor, 0.299.

Since conversion of weight of rubber bromide to weight of rubber is based on an empirical factor, it was necessary to establish this factor for rubber from different sources. Effects of variations in conditions were studied to determine the limits within which it is possible to use the established factor.

EXPERIMENTAL

Samples of rubber bromide for ultimate analysis were prepared by the bromination of benzene solutions of rubber derived from various *Cryptostegia*, guayule, and *kok-saghyz* products. Benzene solutions of the rubber of each plant species were obtained as benzene extracts of the acetone-extracted plant tissues, solutions of the resin-containing crude rubber, milled, or extracted from the plants, or extracts of latices or plant liquors prepared from the plants.

Accurately measured volumes of such rubber solutions containing between 2 and 2.5 mg. of rubber per ml. were brominated at room temperature by adding 1 ml. of the brominating solution (see reagents) for every 10 ml. of rubber solution. Bromination was stopped and the bromide precipitated at the end of an hour by the addition of 30 ml. of absolute alcohol for every 10 ml. of the brominated mixture. The bromide was allowed to settle for 2 hours and was then filtered, washed with absolute alcohol, and dried to constant weight at 50° C. in vacuo. The dried precipitates were analyzed for carbon and hydrogen and in some cases for bromine. When the bromide was separated by filtration from the mother liquor immediately after precipitation, the weight and composition of the recovered bromide were the same as those of the bromide separated after standing for 2 hours.

All analyses of carbon, hydrogen, and bromine were made by common microprocedures. Many analyses were made of bromides prepared from resin-free solvent-extracted rubber, crude rubber, and rubber latex obtained from each of the three plant

Table I. Composition of Rubber Bromides* from Three Plant Sources

Plant Source	Product from Which Prepared	Bromine, %	Carbon, %	Hydrogen, %	Sum of C + H, %	Total, %
Guayule	Latex dispersion	...	25.9	3.4	29.3	..
	Crude rubber	...	25.3	3.5	28.8	..
	Acetone-extracted plant tissue	69.8	25.9	3.5	29.4	99.2
Av.			25.7	3.5	29.2	
Kok-saghyz	Crude rubber	69.9	25.7	3.2	28.9	98.8
	Acetone-extracted plant tissue	70.4	25.9	3.3	29.2	99.6
	Av.		25.8	3.2	29.0	
Cryptostegia	Crude rubber	69.2	27.0	3.4	30.4	99.6
	Acetone-extracted plant tissue	69.9	26.9	3.4	30.3	100.2
	Av.		26.9	3.4	30.3	
Theoretical composition of $C_5H_6Br_2$		70.12	26.34	3.54	29.88	

* Each value is average of values obtained in three to eight determinations.

Table II. Effect of Volume Ratio of Brominating Reagent to Rubber-Benzene Solution on Weight of Rubber Precipitated

Br Solution per 10 Ml. of Rubber-Benzene Solution Ml.	Kok-saghyz		Guayule	
	Rubber bromide from 20 ml. of rubber-benzene	Wt. of rubber calculated ^a	Rubber bromide from 20 ml. of rubber-benzene	Wt. of rubber calculated ^b
	Grams	Grams	Grams	Grams
1	0.1133	0.0329	0.1327	0.0387
2	0.1124	0.0326	0.1345	0.0393
3	0.1135	0.0329	0.1348	0.0394
4	0.1145	0.0332	0.1355	0.0396
5	0.1159	0.0336	0.1350	0.0394
6	0.1143	0.0331	0.1363	0.0398

^a Gravimetric factor 0.290.

^b Gravimetric factor 0.292.

sources. The average values in Table I were obtained by three to eight determinations of bromides from each source.

The sums of the averages of the carbon and-hydrogen content give the factors for converting weights of rubber bromides to weights of rubber. The factors obtained are as follows:

Guayule	0.292
Kok-saghyz	0.290
Cryptostegia	0.303

A mean deviation of ± 0.003 for each of the three factors was obtained when the carbon and hydrogen data for all the samples were analyzed. In general usage it is not necessary to employ the two factors, 0.292 and 0.290, for guayule and kok-saghyz, respectively, but rather to use the average factor, 0.291, whose mean deviation is within the limits of experimental error.

As an additional test of the variation of the gravimetric factor for rubber in rubber bromide, many of the benzene-rubber extracts obtained in the course of plant analyses were analyzed for rubber both by the bromination procedure and by weighing the rubber film obtained by evaporation. Ultimate analyses showed that the films were 98 to 99% pure. The gravimetric factors were determined by dividing the weight of the rubber film by the weight of the rubber bromide. The average of more than one hundred such determinations yielded the following factors: guayule, 0.292 ± 0.003 ; kok-saghyz, 0.290 ± 0.004 ; and Cryptostegia, 0.302 ± 0.003 . All are in close agreement with the values obtained by the ultimate analysis of the bromides (Table I). Preliminary experiments have indicated that this method is applicable to Hevea and that the factor 0.291 gives satisfactory results. In addition, test analyses on a sample of GR-S synthetic rubber indicated that reliable results are obtainable using an experimentally found factor of 0.342.

To evaluate variations in time, temperature, rubber concentration, and bromine concentration which would not significantly

alter the factor, the weights of bromide recovered from aliquots of rubber-benzene solutions brominated under various conditions were compared. Table II shows the effect of varying the volume ratio of the brominating solution to the rubber-benzene solution.

Although there is a slight increase in the weight of rubber bromide formed with increased amounts of the brominating solution, the weights of rubber, calculated by the factor previously established by ultimate analyses, are fairly constant. Since the variation caused by increasing amounts of brominating reagent is small, the procedure adopted has been to use 1 ml. of reagent for every 10 ml. of rubber-benzene solution. The gravimetric factors have been established on the basis of this ratio. To change the ratio would necessitate establishing new factors which would be even further from the theoretical value of 0.299.

To show the effect of varying rubber concentration on the amounts of rubber calculated from the bromide with the established factor, a series of 10-ml. aliquots of a rubber-benzene solution was diluted with different amounts of benzene. These were brominated by the addition of 1 ml. of brominating solution for every 10 ml. of the rubber-benzene solutions. Table III shows the results.

It is evident that rubber-benzene solutions containing 0.5 to 3.0 mg. of rubber per ml. of solution can be analyzed by this procedure, with a recovery of 98 to 100%. For solutions containing much more than 3.0 mg. of rubber per ml., low values were obtained.

Aliquots of benzene solutions of rubber from three plant sources were brominated at room temperature ($25^\circ \pm 2.5^\circ \text{C.}$) and in a refrigerator at 4°C. for periods ranging from 1 to 24 hours. One milliliter of brominating reagent was used for every 10 ml. of rubber-benzene solution. Table IV shows the results.

The data indicate that reasonable variations in time and temperature of bromination from the one hour and room temperature of the described procedure cause insignificant changes in the amounts of rubber calculated from the bromides. However, prolonged bromination at room temperature results in a gradual increase in the weight of the precipitate; this is presumably due to substitution of bromine. At 4°C. the same phenomenon occurs, but, as would be expected, the rate is slower. When brominations were made at -4°C. in carbon tetrachloride solution containing a trace of alcohol, the gravimetric factors calculated for rubber in rubber bromide formed approached the theoretical value. The proposed method of brominating at room temperature is preferred, however, because of its ease of operation, its adaptability, and the accuracy obtainable.

Results of the carbon and hydrogen analyses of the bromides indicate that the gravimetric factors for converting weights of bromide to weights of rubber vary from one plant source to another. The cause of these variations has not been determined; they may be due to the inherent nature of the rubbers. That the bromide method accounts for all the rubber in a solution is

Table III. Analysis of Solutions of Different Rubber Concentrations

Guayule			Kok-saghyz			Cryptostegia		
Mg. of Rubber per 10 Ml. of Rubber-Benzene Solution	% Recovery		Mg. of Rubber per 10 Ml. of Rubber-Benzene Solution	% Recovery		Mg. of Rubber per 10 Ml. of Rubber-Benzene Solution	% Recovery	
Added	Found ^a		Added	Found ^a		Added	Found ^a	
6.6	6.6	100	5.6	5.6	100	5.4	5.4	100
7.9	7.8	99	6.6	6.6	100	6.5	6.5	100
9.9	9.7	98	8.2	8.2	100	8.2	8.1	99
13.2	13.1	99	10.9	10.7	98	10.9	10.8	99
19.8	19.6	99	16.4	16.4	100	16.3	16.1	99
29.7	29.5	99	24.6	24.5	100	24.5	23.9	98
39.5	37.4	95	32.8	31.9	97	32.6	31.5	97

^a Gravimetric factors: guayule, 0.292; kok-saghyz, 0.290; Cryptostegia, 0.303. 1 ml. of brominating reagent added for each 10 ml. of rubber-benzene solution.

Table IV. Effect of Time and Temperature of Bromination on Weight of Rubber Found

Time of Bromination Hours	Weight of Rubber Calculated* from Bromide Precipitated from 20 ML. of Solution					
	Cryptostegia		Kok-saghyz		Guayule	
	Room temp. Gram	4° C. Gram	Room temp. Gram	4° C. Gram	Room temp. Gram	4° C. Gram
1	0.0162	0.0162	0.0276	0.0271	0.0405	0.0402
3	0.0164	0.0166	0.0282	0.0275	0.0418	0.0408
6	0.0178	0.0172	0.0284	0.0277	0.0427	0.0414
24	0.0184	0.0177	0.0285	0.0278	0.0442	0.0427

* Previously established factors for bromination at room temperature for 1 hour were used.

indicated by the close agreement between the weights of rubber calculated by these gravimetric factors and the weights obtained by evaporation of the pure rubber benzene extracts. This agreement does not preclude the possibility of obtaining high rubber values by the bromide method from impure benzene extracts. However, the possibility is remote that any nonrubber plant materials are present which are soluble in benzene and also form alcohol-insoluble bromine derivatives. Added antioxidants and solution aids have never interfered.

REAGENTS

Alcohol, A.C.S., absolute
Acetone, A.C.S., analytical reagent grade
Benzene, A.C.S., analytical reagent grade
Trichloroacetic acid, Eastman Kodak Company White Label
Benzene containing 1% trichloroacetic acid
Brominating solution. Dissolve 2 grams of iodine in 100 ml. of carbon tetrachloride, filter through filter paper, and add 5 ml. of bromine to the filtrate.

ANALYTICAL PROCEDURES

Determination of rubber by the bromide method is useful in evaluating the rubber content of benzene extracts of plant tissues, crude rubbers isolated from plants by mechanical or chemical means, and rubber-containing liquors and lattices.

DETERMINATION OF RUBBER IN THE ORGANIC SOLVENT EXTRACT OF PLANT TISSUE. An organic solvent extract or the rubber film obtained by evaporating an extract may be analyzed by the bromide procedure.

To analyze a rubber film, redissolve it in benzene by stirring and gentle heating, cool, and make to volume in a volumetric flask with benzene. Choose as the final volume of either the extract or the redissolved film one which will contain 0.5 to 3.0 mg. of rubber per ml. Transfer to a beaker an aliquot containing a minimum of 25 mg. of rubber, and add 1 ml. of the brominating solution for each 10 ml. of the aliquot. Cover the beaker with a watch glass and let stand at room temperature for one hour to permit agglomeration of the particles. At the end of the hour stir the brominated mixture thoroughly with a glass rod, taking special care to loosen any precipitate from the bottom of the beaker. Add absolute alcohol, with constant stirring, in the ratio of 30 ml. of alcohol for each 10 ml. of the brominated mixture. Allow the bromide precipitate to settle for at least one hour and then filter with suction, using a tared Gooch crucible with asbestos pad. An ordinary rubber policeman and alcohol may be used in transferring the bromide and in washing the beaker. Wash the bromide several times with alcohol, dry at 50° C. in vacuo under 5-mm. mercury pressure, cool, and weigh. Calculate the rubber content from the weight of the rubber bromide by the following gravimetric factors: 0.290 for kok-saghyz, 0.292 for guayule, and 0.303 for Cryptostegia.

DETERMINATION OF RUBBER IN RUBBER CRUDES. Prepare the analytical sample of the crude rubber by passing it several times through compounding rolls, finally mill it into a thin ribbonlike sheet, and from this cut or tear narrow strips for moisture and for rubber analysis.

Determine the moisture by drying approximately 2 grams of the crude rubber in vacuo at 50° C. to constant weight (12 hours).

Solution of the sample for rubber analysis may be obtained either by heating it in benzene or by allowing it to stand at room temperature in a 1% solution of trichloroacetic acid in benzene. Although the latter method requires 2 to 3 days for solution, it is more convenient in routine analysis, and in general less time-consuming. Since determination of the benzene-insoluble and acetone-insoluble content of the crude rubber is usually required in addition to rubber hydrocarbon, samples of approximately 0.5 grams are recommended.

Cut or tear approximately 0.5 gram of the milled sheet into fine strips, weigh to the nearest 0.1 mg., and place in a tared 70-ml. centrifuge tube. Add 50 ml. of a 1% solution of trichloroacetic acid in benzene, insert a glass stirring rod, lightly stopper the tube with a plug of cotton, and allow it to stand at room temperature for 3 days. To aid in the complete solution of the rubber, stir two or three times a day during the 3-day interval. Centrifuge to separate the benzene-insolubles and decant the benzene-rubber solution into a 200-ml. volumetric flask. Wash the benzene-insolubles and the centrifuge tube twice with 50-ml. portions of benzene, centrifuging after each wash. Add the benzene washes to the benzene-rubber solution and dilute to 200 ml. with benzene. Determine the rubber in a 20-ml. portion of this solution by the bromide method described in the previous section. Calculate the per cent rubber in the crude by the equation:

$$\% \text{ rubber} = \frac{\text{gravimetric factor} \times \text{weight of bromide (g.)} \times \text{volume of sample (200 ml.)} \times 100}{\text{weight of crude rubber (grams)} \times \frac{100 - \% \text{ moisture}}{100} \times \text{portion used (20 ml.)}}$$

If the percentage of acetone-soluble or resin fraction and the percentage of those materials insoluble in both acetone and benzene are desired, determine the insolubles directly and calculate the acetone-solubles by difference. To determine the insoluble fraction, thoroughly wash the benzene-insoluble residue left in the centrifuge tube with acetone, separate the insolubles by centrifuging, and discard the acetone wash solution. Dry the residue in the tared centrifuge tube for one hour at 110° C. in an air oven, cool, weigh, and calculate the per cent insolubles on a moisture-free basis.

The per cent acetone-soluble fraction is obtained by subtracting the sum of the percentages of moisture-free rubber and insolubles from 100. Since the proposed method is especially suited to the analysis of crude rubber and is applicable to samples containing either large or small amounts of nonrubber nonresin materials, several typical analyses of samples of such rubber from different plants are given in Table V. These show the reproducibility of the method.

DETERMINATION OF RUBBER IN AQUEOUS LIQUORS LOW IN RUBBER CONTENT. Many types of aqueous rubber-containing emulsions having rubber contents ranging from less than 1 to about 5% may be conveniently analyzed for rubber by the bromide procedure. Benzene extracts of the rubber in such emulsions are most easily prepared in the Waring Blendor. The

Table V. Analyses of Crude Rubber from Different Plants

Plant Source	Sample No.	% Rubber		% Insolubles (Benzene and Acetone)		Acetone-Solubles* (Resins)
Guayule	5293	65.0	65.1	15.3	15.3	19.7
	5319	78.6	79.2	5.3	5.3	15.9
	5341	68.2	68.0	10.4	10.3	21.6
	5564	73.8	73.9	7.2	7.3	18.9
	5568	77.4	77.5	1.8	1.8	20.8
Kok-saghyz	7510	80.9	80.9	6.4	6.9	12.5
	7520	86.2	86.1	7.2	7.2	6.7
	7579	77.3	76.8	8.0	8.0	15.0
	8088	79.0	78.7	7.1	7.4	13.9
	8227	77.5	77.5	9.7	9.9	12.7
Cryptostegia	7726	64.5	65.3	1.1	1.0	34.1
	9040	87.4	87.2	5.2	5.3	7.5
	9050	63.1	63.3	28.1	28.1	8.7
	9054	51.3	51.2	40.5	40.3	8.4
	9060	84.6	84.4	5.4	5.3	10.2

* Calculated by difference from average of both rubber and insolubles.

persistent emulsions which result when alkali-stabilized rubber liquors are extracted with benzene in the Blendor can be avoided by acidifying the liquor with concentrated hydrochloric acid preliminary to the extraction.

To determine the rubber content, transfer 10 to 50 ml. of the emulsion to a Waring Blendor using a transfer pipet, rinse the pipet several times with water, and combine the rinses with the measured sample, making a total volume of approximately 75 ml. Add sufficient concentrated hydrochloric acid to break the emulsion; usually 5 to 10 ml. are required. Then add about 180 ml. of benzene, churn for 2 minutes, wash the emulsion into a 500-ml. separatory funnel with water, and allow to stand until the aqueous layer appears clear, usually about 8 hours. Draw off and discard the clear aqueous layer.

Transfer the benzene and the interface layers to centrifuge tubes, centrifuge until separation into layers is complete, and transfer the benzene layer to a 400-ml. beaker using a pipet and suction. Rinse the separatory funnel with benzene. Add the rinses to the aqueous residue in the centrifuge tube, mix well, and centrifuge. Again draw off the benzene layer and add it to the original benzene solution in the beaker. Concentrate on a steam bath, transfer, and make to the mark in a volumetric flask of such volume that 20 ml. of the final volume will contain between 10 and 60 mg. of rubber. Transfer a 20-ml. aliquot to a 250-ml. beaker and brominate by the previously described procedure. Should the 20-ml. aliquot of the original solution contain more than 60 mg. of rubber, dilute to the desired concentration and brominate a 20-ml. portion. When the total benzene extract is very low in rubber, it may be reduced to 20 ml. and brominated in its entirety. Calculate the rubber content from the equation:

$$\text{Mg. of rubber/ml.} = \frac{\text{gravimetric factor} \times \text{weight of bromide (mg.)} \times \text{dilution factor}}{\text{ml. of sample}}$$

DETERMINATION OF RUBBER IN LATEX OR LIQUOR OF HIGH RUBBER CONTENT. When concentrated rubber liquors (containing more than 5% rubber) and latices are being analyzed, complete extraction of the rubber by benzene cannot be achieved by the Waring Blendor method described above. Instead, benzene is added to the sample, the mixture is acidified, and the water is removed by distillation in a Bidwell-Sterling type moisture

apparatus. This results in a water-free solution of the rubber benzene.

Weigh by difference from a glass-stoppered vial that amount of the well-mixed sample which contains less than 1.5 grams of rubber and transfer to a 500-ml. volumetric (boiling) flask equipped with a 24/40 outer joint. Acidify the sample with concentrated hydrochloric acid to give an acid concentration of about 10%, then add 200 ml. of benzene and attach the flask to a Barrett type Bidwell-Sterling moisture test apparatus provided with a condenser. Boil the mixture until all water is removed (water level in the trap remains constant), and a clear benzene solution is obtained. Remove the flask from the apparatus, cool, and dilute to the mark with benzene. Transfer, with a pipet, a 50-ml. aliquot to a 600-ml. beaker and determine the rubber in this aliquot by the bromide method and the following equation:

$$\% \text{ rubber} = \frac{\text{Gravimetric factor} \times \text{weight of bromide (grams)} \times \text{volume of sample (500 ml.)} \times 100}{\text{weight of sample} \times \text{aliquot (50 ml.)}}$$

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